Expt1. Equilibrium Lattice Constants and Bulk Moduli

1 PURPOSE

Calculate the equilibrium lattice constants and bulk moduli of given five elements;

Calculate the equilibrium lattice constant and bulk modulus of Al with BCC structure.

2 PRINCIPLE

2.1 LATTICE CONSTANT

The lattice constant, or lattice parameter, refers to the physical dimension of unit cells in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as a, b, and c. However, in the special case of cubic crystal structures, all of the constants are equal and we only refer to a.

2.2 BULK MODULUS

The bulk modulus is defined by

$$B \equiv -\frac{dP}{dV/V} \tag{2-1}$$

where V is the volume of a cubic unit cell and P the pressure.

The cohesive energy (E, or binding energy) per atom can be calculated (e.g., via LAMMPS) as a function of the lattice parameter, a. For a cubic cell, the total energy is given by ε=ME, where M is the number of atoms in the unit cell the volume of which is given by $V=a^3$.

Pressure is given by

$$\mathrm{P} = -\frac{d\varepsilon}{dV} = -\frac{M}{3a^2}\frac{dE}{da} \tag{2-2}$$

and the bulk modulus

$$\mathrm{B} = \frac{M}{9a_0}\frac{d^2E}{da^2}\Big|_{a_0} \tag{2-3}$$

where a_0 is the equilibrium lattice parameter corresponding to the minimum of E.

3 PROCEDURE

3.1 COMPUTE THE ENERGY FOR SEVERAL VALUES OF THE VOLUME

(1) Given a lattice constant, generate a 3×3×3 supercell with

a) for BCC (e.g., Fe), 54 atoms;

b) for FCC (e.g., Cu, Al), 108 atoms;

c) for HCP (e.g., Mg), 108 atoms;

d) for Diamond (e.g., Si), 216 atoms.

(2) Compute the energy per atom with the given lattice constant via LAMMPS.

Syntax:

```
$    lmp < in.lattice
```

LAMMPS input script is (e.g., Cu):

```
# -------------- INITIALIZATION ----------------------
variable      i equal 0
variable      iteration equal 40
variable      n loop ${iteration}
label         loopn
# -------------- SET THE ITERATIONS ------------------
variable      i equal $i+1
print         "loop number is $i"
if            "$i==1" then "shell rm data"
# -------------- LATTICE SPACING DELTA ---------------
variable      delta equal 0.001
boundary      p p p
units         metal
atom_style    atomic
timestep      0.005
# -------------- ESTIMATE OF LATTICE CONSTANT --------
variable      Lattice_Guess equal 3.61
variable      spacing equal ${Lattice_Guess}+${delta}*($i-${iteration}/2)
lattice       fcc ${spacing}
# -------------- CREATE THE BOX AND ATOMS ------------
region        box block 0 3 0 3 0 3
create_box    1 box
create_atoms  1 box
# -------------- SET POTENTIAL -----------------------
pair_style    eam/alloy
pair_coeff    * * jin_copper_lammps.setfl Cu
# -------------- WRITE CFG FILES ---------------------
run           0
variable      PotentialEnergy equal pe
variable      Natoms equal atoms
variable      E_per_Atom equal ${PotentialEnergy}/${Natoms}
dump          1 all cfg 1000 a*.cfg mass type xs ys zs
dump_modify   1 element Cu
# -------------- PRINT DATA --------------------------
```

```
fix           extra all print 1 "${spacing} ${E_per_Atom}" append data
run           1
# -------------- JUMP TO THE NEXT ITERATION ----------
clear
next          n
jump          in.lattice loopn
```

(3) Loop with different lattice constant. After the run, LAMMPS outputs “data” file with two columns: Lattice constant (Å) and Energy per atoms (eV).

By default, LAMMPS creates neighbor lists, computes forces, and imposes fix constraints before every run. And after every run it gathers and prints timing statistics.

LAMMPS output:

File	Description
log.lammps	log file for a LAMMPS run
a0.cfg	atomic configuration (AtomEye)
data	spacing & energy data (Gnuplot)

3.2 FITTING EXPERIMENTAL DATA

Plot LAMMPS output with Gnuplot:

(1) Second degree polynomial equation fitting

Syntax:

```
$   gnuplot plot.2nd.gnu
```

Input script is:

```
set xlabel "Lattice spacing (Angstrom)"
set ylabel "Energy/atom (eV)"
set title "Lattice spacing and energy"

plot 'data'
f(x)=a*x**2+b*x+c
fit f(x) 'data' via a,b,c
plot 'data',f(x)
```

After the run, Gnuplot outputs the fitting curve and parameters with asymptotic standard error.

(2) The Birch-Murnaghan equation of state fitting

Syntax:

```
$   gnuplot plot.bm.gnu
```

We can use Gnuplot’s fitting routines to make a Birch fit to the FCC, BCC, HCP and diamond data, which will allow us to obtain the equilibrium lattice constants and bulk moduli for these four phases.

Input script is (e.g., FCC):

```
set title "Equation of State of FCC"
set xlabel "Volume/atom (A^3)"
set ylabel "Energy/atom (eV)"
t(vo,v) = (vo/v)**.666666666666666667 - 1.0
e(eo,vo,ko,kop,v) = eo + 1.125*ko*vo*t(vo,v)*t(vo,v)* (1.0 + 0.5*(kop-
4.0)*t(vo,v))
ef = -3.49
vf = 11.7
kf = 0.856
kfp = 4
fit e(ef,vf,kf,kfp,x) "< sed '/^#/d' data | awk '{print ($1)^3/4, $2}'"
via ef,vf,kf,kfp
plot "< sed '/^#/d' data | awk '{print ($1)^3/4, $2}'" t "FCC" w p pt 6,
e(ef,vf,kf,kfp,x) t "Birch fit" w l

print ""
print "Results of 3rd order Birch fit:"
print ""
print "FCC Lattice:"
af = (4.0*vf)**.333333333333333
print ""
print "E_0 = ",ef," eV"
print "a_0 = ",af," Angstrom"
print "V_0 = ",vf," Angstrom**3"
print "B_0 = ",kf*160.2176565," GPa"
print "B_0'= ",kfp
```

3.3 VISUALIZE ATOMIC CONFIGURATION

Use AtomEye or Ovito to view atomic configuration, where AtomEye is the most direct approach.

(1) AtomEye

Syntax:

```
$   A.i686 a0.cfg
```

(2) Ovito

Import CFG files to Ovito.

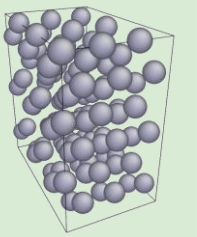
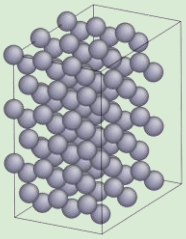
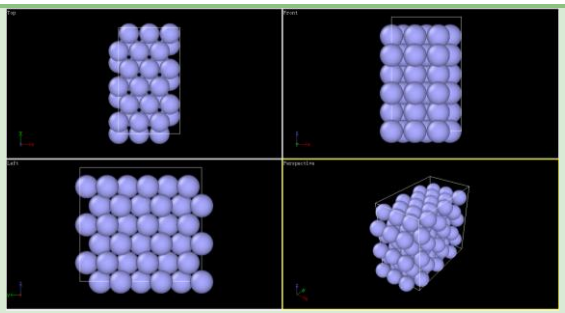
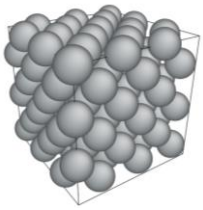
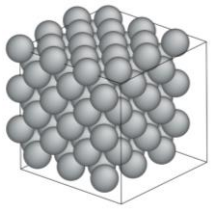
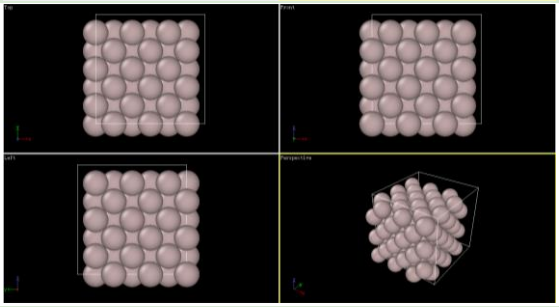
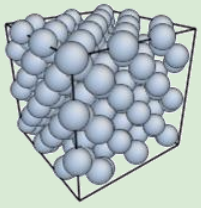
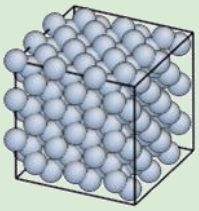
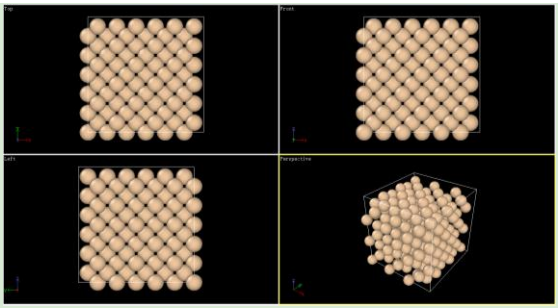
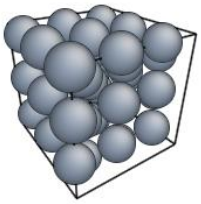
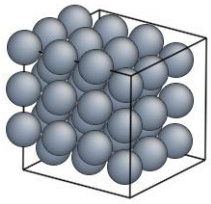
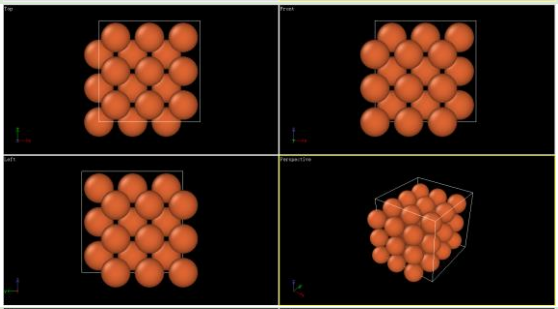
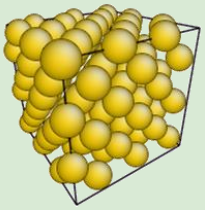
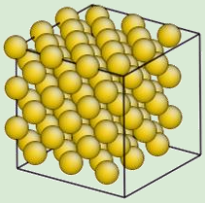
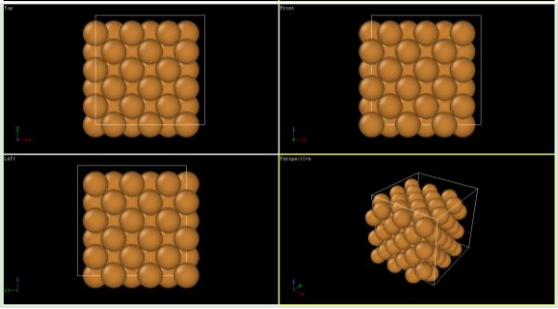
4 RESULTS

The elements and parameters are listed in the following table, where a_0 refers to the estimate of lattice constant.

Element	Structure, M	Expt. a_0 (Å)	Expt. B (Gpa)	a_0 (Å)
Mg	HCP, $4/(\sqrt{3} * c/a)$	3.209, c/a=1.623	35	3.184, c/a=1.628
Al	FCC, 4	4.049	72	4.045
Si	Diamond, 8	5.431	98	5.43
Fe	BCC, 2	2.866	168	2.855
Cu	FCC, 4	3.614	142	3.61

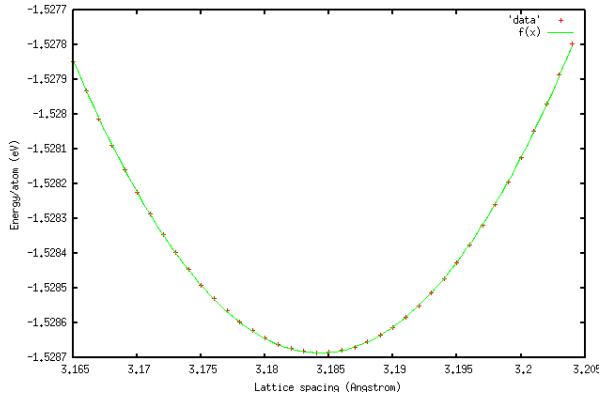
4.1 ATOMIC CONFIGURATION

Atomic configurations of the five elements are listed in the following table, where *Perspective* and *Parallel* are created by AtomEye, and *Three-View* is screenshot of Ovito.

Element	Perspective	Parallel	Three-View
Mg			
Al			
Si			
Fe			
Cu			

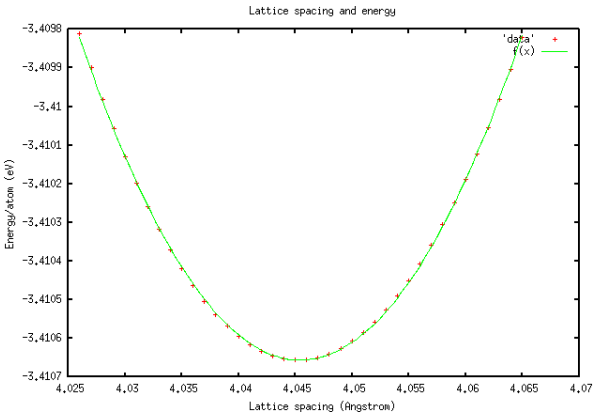
4.2 FITTING CURVE

(1) Second degree polynomial equation fitting



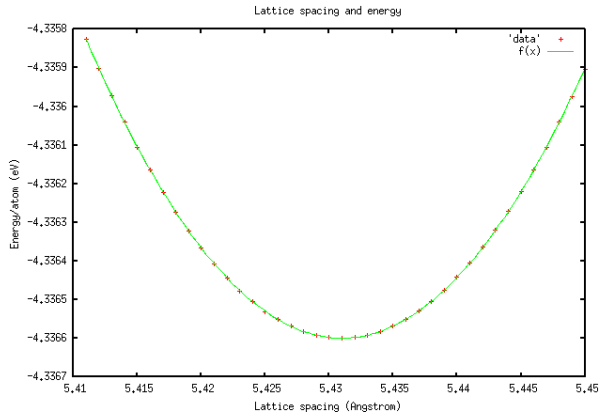
Final set of parameters		Asymptotic Standard Error	
a	= 2.27117	+/- 0.002085	(0.09179%)
b	= -14.464	+/- 0.01328	(0.0918%)
c	= 21.4997	+/- 0.02114	(0.09833%)

(a) Mg



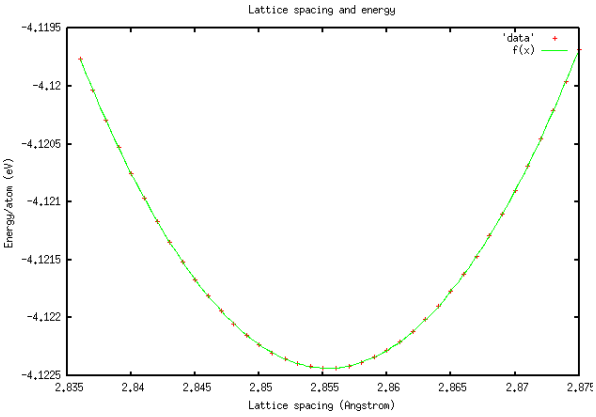
Final set of parameters		Asymptotic Standard Error	
a	= 2.20808	+/- 0.005565	(0.252%)
b	= -17.8654	+/- 0.04503	(0.252%)
c	= 32.7261	+/- 0.09108	(0.2783%)

(b) Al



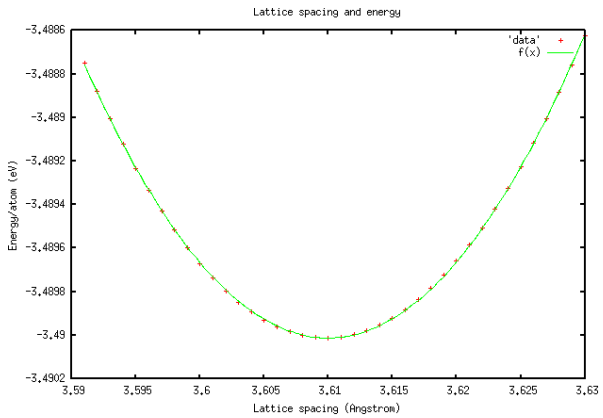
Final set of parameters		Asymptotic Standard Error	
a	= 1.93485	+/- 0.001141	(0.05897%)
b	= -21.0163	+/- 0.01239	(0.05896%)
c	= 52.7331	+/- 0.03365	(0.06381%)

(c) Si



Final set of parameters		Asymptotic Standard Error	
a	= 7.12859	+/- 0.001914	(0.02686%)
b	= -40.7092	+/- 0.01093	(0.02686%)
c	= 53.9969	+/- 0.01561	(0.02891%)

(d) Fe



Final set of parameters		Asymptotic Standard Error	
a	= 3.48337	+/- 0.005239	(0.1504%)
b	= -25.1497	+/- 0.03783	(0.1504%)
c	= 41.9049	+/- 0.06829	(0.163%)

(e) Cu

(2) The B-M equation of state fitting

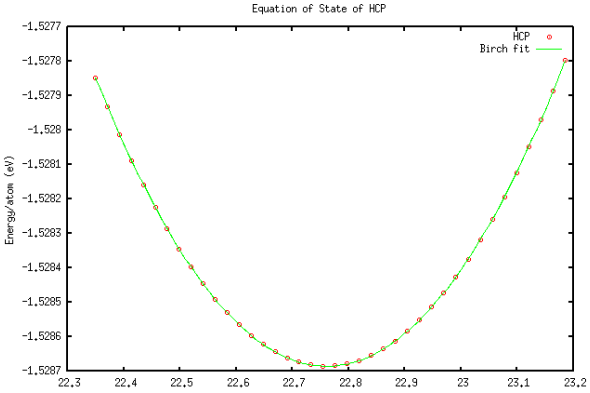
(a) Mg

```
Results of 3rd order Birch fit:

HCP Lattice:

E_0 = -1.52868631023185 eV
a_0 = 3.18431542679217 Angstrom
V_0 = 22.76161517799 Angstrom**3
B_0 = 36.0301849559129 GPa
B_0'= -0.761464207502543
```

Final set of parameters		Asymptotic Standard Error	
ef	= -1.52869	+/- 6.385e-08	(4.177e-06%)
vf	= 22.7616	+/- 4.352e-05	(0.0001912%)
kf	= 0.224883	+/- 3.53e-05	(0.0157%)
kfp	= -0.761464	+/- 0.04939	(6.486%)



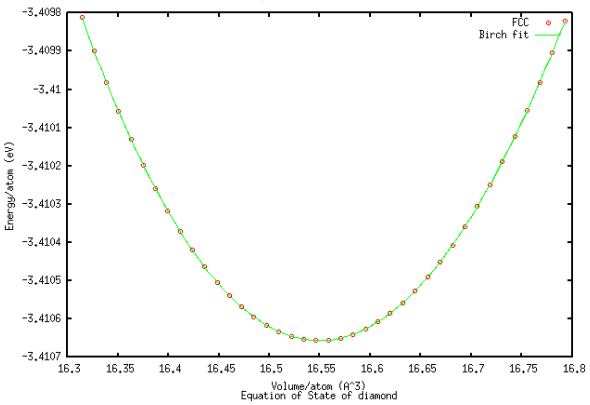
(b) Al

```
Results of 3rd order Birch fit:

FCC Lattice:

E_0 = -3.41065714040381 eV
a_0 = 4.04527130437683 Angstrom
V_0 = 16.5494273213047 Angstrom**3
B_0 = 77.7803912766984 GPa
B_0'= 7.11079881556912
```

Final set of parameters		Asymptotic Standard Error	
ef	= -3.41066	+/- 4.779e-08	(1.401e-06%)
vf	= 16.5494	+/- 1.907e-05	(0.0001152%)
kf	= 0.485467	+/- 5.873e-05	(0.0121%)
kfp	= 7.1108	+/- 0.04824	(0.6784%)



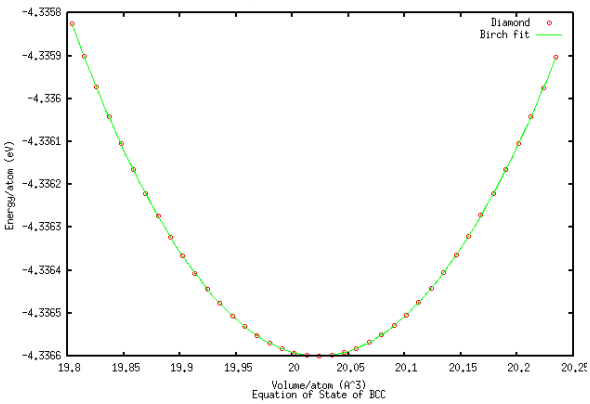
(c) Si

```
Results of 3rd order Birch fit:

diamond Lattice:

E_0 = -4.33660000718975 eV
a_0 = 5.43095170306466 Angstrom
V_0 = 20.0234005455525 Angstrom**3
B_0 = 101.425444944596 GPa
B_0'= 2.85073370817905
```

Final set of parameters		Asymptotic Standard Error	
ef	= -4.3366	+/- 2.503e-08	(5.772e-07%)
vf	= 20.0234	+/- 1.015e-05	(5.071e-05%)
kf	= 0.633048	+/- 4.565e-05	(0.007211%)
kfp	= 2.85073	+/- 0.03823	(1.341%)



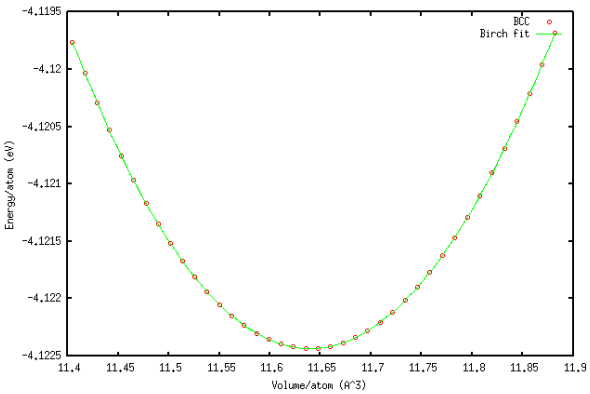
(d) Fe

```
Results of 3rd order Birch fit:

BCC Lattice:

E_0 = -4.1224351934112 eV
a_0 = 2.85532720281661 Angstrom
V_0 = 11.6395892035167 Angstrom**3
B_0 = 177.84840115414 GPa
B_0'= 1.41894857732246
```

Final set of parameters		Asymptotic Standard Error	
ef	= -4.12244	+/- 9.774e-08	(2.371e-06%)
vf	= 11.6396	+/- 1.209e-05	(0.0001039%)
kf	= 1.11004	+/- 8.498e-05	(0.007655%)
kfp	= 1.41895	+/- 0.02161	(1.523%)



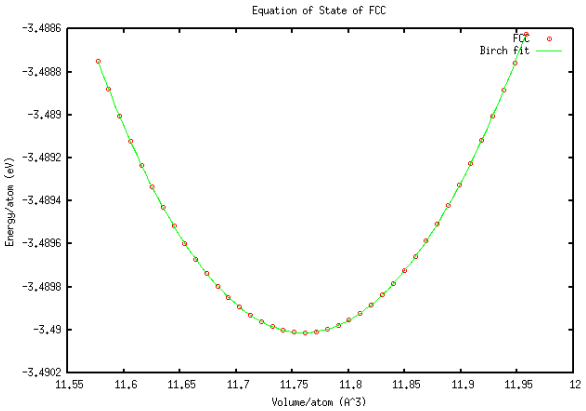
(e) Cu

```
Results of 3rd order Birch fit:

FCC Lattice:

E_0 = -3.49001356518869 eV
a_0 = 3.6098665239098 Angstrom
V_0 = 11.7601656929196 Angstrom**3
B_0 = 137.631357881733 GPa
B_0'= 4.22407949095044
```

Final set of parameters		Asymptotic Standard Error	
==========		==========	
ef	= -3.49001	+/- 6.808e-08	(1.951e-06%)
vf	= 11.7602	+/- 1.373e-05	(0.0001167%)
kf	= 0.859027	+/- 9.505e-05	(0.01106%)
kfp	= 4.22408	+/- 0.03897	(0.9225%)



4.3 *Al (BCC)

(1) Estimate of lattice constant

a) Constant volume model

The volume of unit cell is given by

$$V_0 = {a_0}^3 \tag{4-1}$$

or

$$V_0 = M \cdot V_a \tag{4-2}$$

where V_a refers to volume per atom. Thus

$$V_a = \frac{{a_0}^3}{M} \tag{4-3}$$

In the assumption that volume per atom remains constant, given the lattice constant of FCC Al, we can reach an estimate of lattice constant of BCC Al by

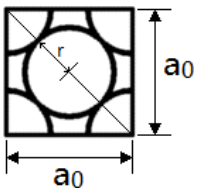
$$\frac{{a_{0BCC}}^3}{M_{BCC}} = \frac{{a_{0FCC}}^3}{M_{FCC}} \tag{4-4}$$

$$\frac{{a_{0BCC}}^3}{2} = \frac{4.045^3}{4}$$

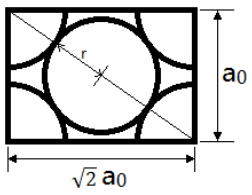
Therefore, the equilibrium lattice constant of BCC Al, $a_{0\,BCC}$ = 3.21 (Å).

b) Rigid sphere model

In the assumption that atoms are tangent to each other, structures of (001) in FCC and (011) in BCC unit cell are



(001) in FCC



(011) in BCC

For radius of Al atoms is constant, an estimate of lattice constant of BCC Al is given by

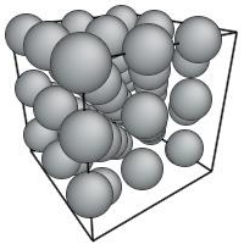
$$\sqrt{3} \cdot a_{0_{BCC}} = \sqrt{2} \cdot a_{0_{FCC}} \tag{4-5}$$

Thus the equilibrium lattice constant of BCC Al, $a_{0\,BCC}$ = 3.30 (Å).

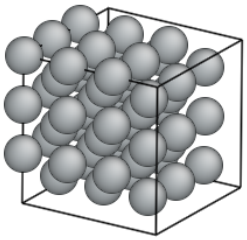
In conclusion, the equilibrium lattice constant of BCC Al is probably between 3.21 (Å) ~ 3.30 (Å). After several trials, an estimate of 3.238 (Å) is proper.

(2) Atomic configuration

a) AtomEye

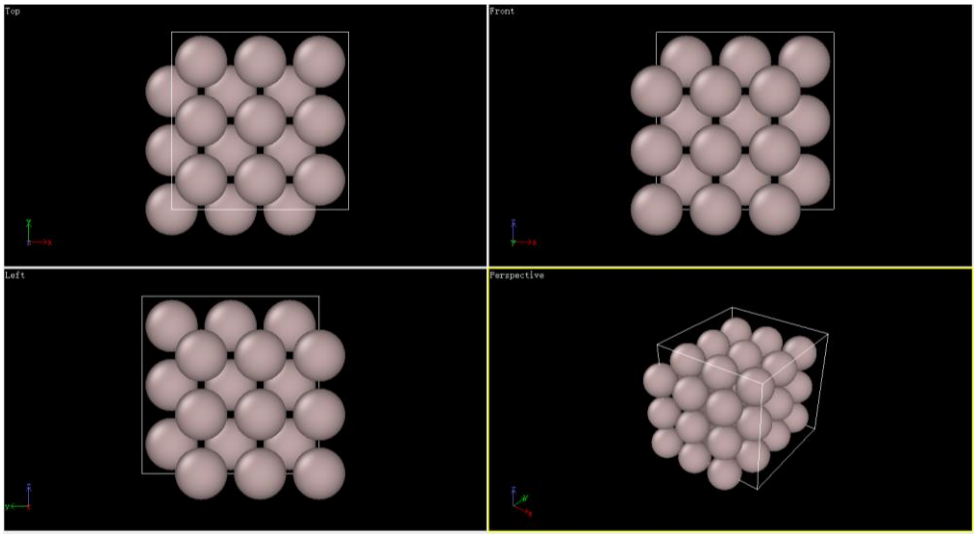


Perspective



Parallel

b) Ovito

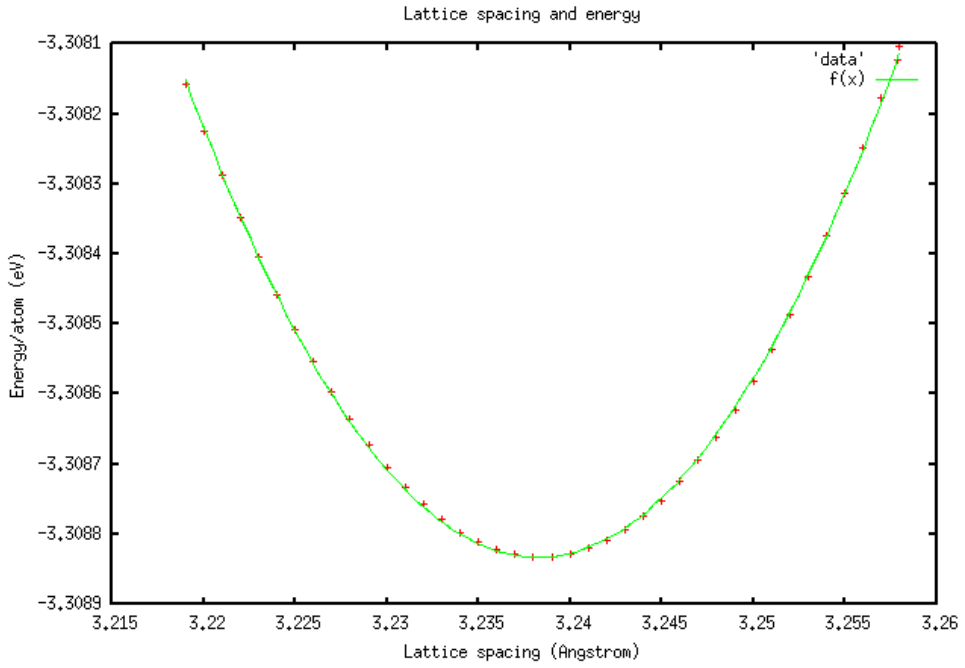


(3) Fitting curve

a) Secondary degree polynomial equation fitting

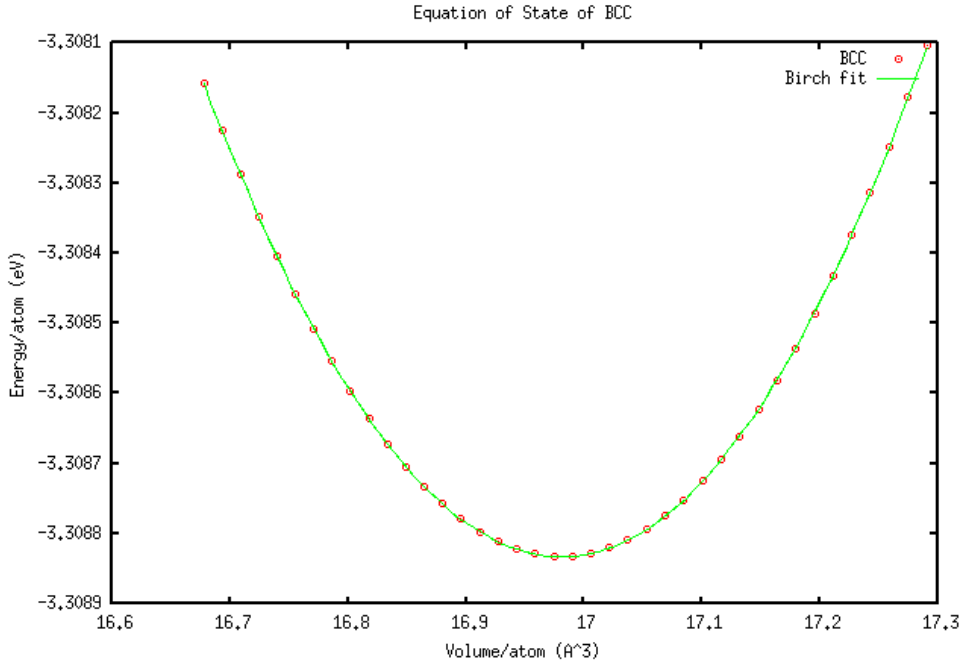
```
Final set of parameters            Asymptotic Standard Error
=======================            ==========================

a               = 1.84574          +/- 0.00445      (0.2411%)
b               = -11.9539         +/- 0.02882      (0.2411%)
c               = 16.0459          +/- 0.04667      (0.2908%)
```



b) The B-M equation fitting

Final set of parameters		Asymptotic Standard Error	
ef	= -3.30883	+/- 6.349e-08	(1.919e-06%)
vf	= 16.981	+/- 3.908e-05	(0.0002301%)
kf	= 0.253454	+/- 4.876e-05	(0.01924%)
kfp	= -3.70009	+/- 0.06127	(1.656%)



```
Results of 3rd order Birch fit:

BCC Lattice:

E_0 = -3.30883332765408 eV
a_0 = 3.23840582898356 Angstrom
V_0 = 16.9810218945939 Angstrom**3
B_0 = 40.6077685020645 GPa
B_0'= -3.70009213960537
```

4.4 CONCLUSION

To calculate equilibrium lattice constants and bulk moduli, while they are obtained directly using the Birch-Murnaghan equation of state fitting, in the case of second degree polynomial equation fitting, for equilibrium lattice constant is given by

$$\left.\frac{dE}{da}\right|_{a_0} = 0 \tag{4-6}$$

where

$$E = a \cdot \boldsymbol{a}^2 + b \cdot \boldsymbol{a} + c \tag{4-7}$$

thus lattice constants

$$a_0 = -\frac{b}{2a} \tag{4-8}$$

and bulk moduli can be derived from (2-3).

The equilibrium lattice constants and bulk moduli are listed in the following table.

Element	Expt. a_0 (Å)	Expt. B (Gpa)	2nd. a_0 (Å)	2nd. B (Gpa)	B-M. a_0 (Å)	B-M. B (Gpa)
Mg	3.209	35	3.184	36.0	3.184	36.0
Al	4.049	72	4.045	77.7	4.045	77.8
Si	5.431	98	5.431	101.5	5.431	101.4
Fe	2.866	168	2.855	177.8	2.855	177.8
Cu	3.614	142	3.610	137.4	3.610	137.6
Al (BCC)	–	–	3.238	40.6	3.238	40.6

Variance analysis:

Element	2nd. Δa_0 (Å)	2nd. Δa_0%	2nd. ΔB (Gpa)	2nd. ΔB%	B-M. Δa_0 (Å)	B-M. Δa_0%	B-M. ΔB (Gpa)	B-M. ΔB%
Mg	-0.025	-7.79	1.0	2.86	-0.025	-7.79	1.0	2.86
Al	-0.004	-0.10	5.7	7.92	-0.004	-0.01	5.8	8.06
Si	-0.000	-0.00	3.5	3.57	-0.000	-0.00	3.4	3.47
Fe	-0.011	-0.38	9.8	5.83	-0.011	-0.38	9.8	5.83
Cu	-0.004	-0.11	-4.6	-3.24	-0.004	-0.11	-4.4	-3.20

5 DISCUSSION

By comparison, we can find that

(a) equilibrium lattice constants and bulk moduli given by second degree polynomial fitting and B-M equation of state fitting are nearly equal;

(b) equilibrium lattice constants of simulation are all smaller than that of experiment, while

(c) bulk moduli of simulation are larger, except Cu, than that of experiment.

The difference stated in "(b)" is probably related to the number of atoms within cutoff distance, or potential function used to compute interaction forces.

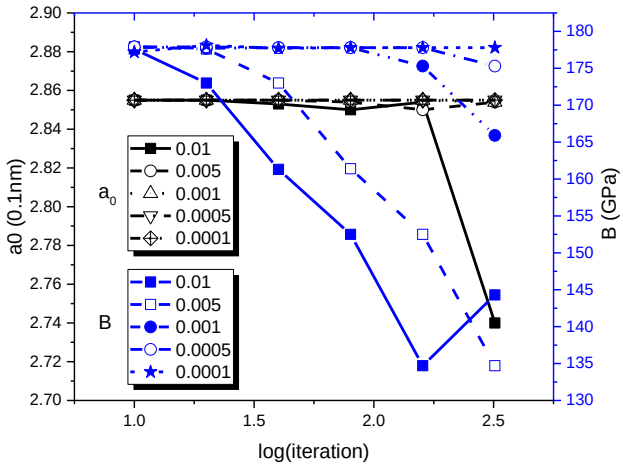
Considering the case of Si, lattice constant of simulation is equal to that of experiment, though bulk moduli are different. Therefore, the difference stated in "(c)" may be caused by the inaccuracy of bulk modulus formulas.

To verify these assumptions, as far as Fe is concerned, a series of iteration times and lattice constant interval are applied to simulation. The equilibrium lattice constants and bulk moduli are listed in the following table, which are given by the B-M equation of state fitting.

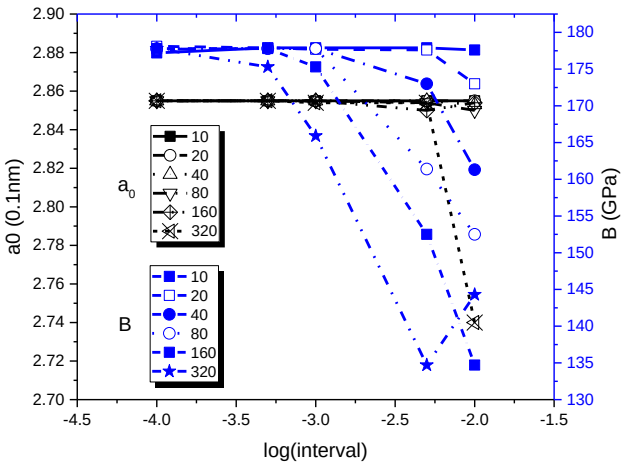
a_0 (Å), B (Gpa)

iteration / interval	10	20	40	80	160	320
0.01	2.855, 177.6	2.855, 173.0	2.853, 161.3	2.850, 152.5	2.854, 134.7	2.740, 144.3
0.005	2.855, 177.9	2.855, 177.6	2.855, 173.0	2.854, 161.4	2.850, 152.5	2.854, 134.7
0.001	2.855, 177.9	2.855, 177.7	2.855, 177.8	2.855, 177.8	2.855, 175.3	2.854, 165.9
0.0005	2.855, 177.9	2.855, 177.9	2.855, 177.8	2.855, 177.8	2.855, 177.8	2.855, 175.3
0.0001	2.855, 177.2	2.855, 178.1	2.855, 177.7	2.855, 177.8	2.855, 177.8	2.855, 177.8

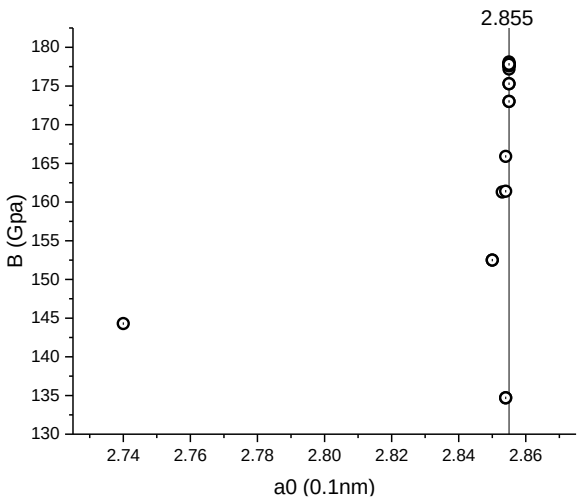
Plot data:



Fixed Interval



Fixed Iteration



Analysis:

I. Equilibrium lattice constants have little variance, except when interval and iteration times are both large. Further experiment is needed to see whether it is cutoff distance or potential function that leads to the inaccuracy of lattice constants.

II. Bulk moduli decrease with the increase of iteration times or lattice constant interval. An additional simulation is conducted (iteration times = 2000, lattice constant interval = 0.00001). The result is (2.855, 177.8), and data fit well, indicating the fitting equation is accurate.

III. Mark the points of different parameters in a single B-a_0 plot. While bulk moduli appear dispersive, equilibrium lattice constants are close to but not exceed 2.855, except one point at 2.740, which occurred at the maximum of iteration times and lattice constant interval.

Actually, interval indicates the precision of fitting, which increases when interval is reduced. However, the influence of initial value also increases if interval is too small.

And iteration times plays different roles depending on interval: a) When interval is small, a large iteration times adds more points for fitting, increasing the accuracy of fitting curves; b) When interval is large, a large iteration times expands the range of fitting. However, lattice constants and bulk moduli are calculated only refers to the bottom of fitting curves, which distorts when the range is too wide.

Therefore, a moderate lattice constant interval with large iteration times is ideal.